Solid Oxide Cell and Stack Testing, Safety and Quality Assurance

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Test Module 04: Electrochemical Impedance Spectroscopy

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Abbreviations

AC	Alternating current
ASR	Area specific resistance
DC	Direct current
ECM	Equivalent circuit model
nlpm	Normal litre per minute
OCV	Open circuit voltage
RU	Repeating unit
SOC	Solid oxide cell
SOFC	Solid oxide fuel cell
SOEC	Solid oxide electrolysis cell
slpm	Standard litre per minute
TIP	Test input parameter
TM	Test module
TOP	Test output parameter

TM 04 – Electrochemical Impedance Spectroscopy

1 Objective and Scope

Electrochemical impedance spectroscopy (EIS) is an important tool to analyze processes taking place in electrochemical systems like fuel/electrolysis cells and stacks. It shows the different frequency dependent impedances of a test object which can either be a cell, a repeat unit of a stack or a complete stack. Moreover, it is used to understand the behaviour of the resistances of the cell/stack test object, e.g, the ohmic resistance, the polarization resistances of the electrodes and the gas conversion resistances.

However, there are only few documents on test procedures for this measurement method [1], [2]. Therefore, this test module contains important information on electrochemical impedance measurement and the resulting impedance spectra of SOC cells and stacks for both electrolysis and fuel cell modes. All important test parameters and conditions as well as a description on how to perform an impedance measurement are included in this test module. Additionally it provides information about the evaluation and analysis of the results.

Possible test objects which may be examined by electrochemical impedance spectroscopy are detailed shown in figures 4 and 5 of chapter 6.2 “Interface between test object and test environment” of TM 00 “General SOC Testing Guidelines” [3]. TM 00 also includes a comprehensive “list of quantities” including all symbols used in this test module.

2 Basic Principles

The fundamental approach of electrochemical impedance spectroscopy (EIS) is to apply a sinusoidal excitation signal with small amplitude to the system under investigation and measure the corresponding response signal (Figure 1). If the system satisfies contemporaneously the conditions of causality, linearity and time-invariance, the response to a sinusoidal current is a sinusoidal voltage and vice versa, both sharing the same frequency:

Input Signal: $$I(\omega,t) = \bar{I}\sin(\omega t) \quad (1)$$

with $$\omega = 2\pi\upsilon \quad (2)$$

An electrochemical system, e.g. a fuel or electrolysis cell/stack assembly, usually consists of elements with capacitive, inductive and/or resistive behaviour, which create phase angles/shifts between the alternating excitation signal and the corresponding response signal. Thus, the output signal can be formulated as follows:

Output Signal: $$V(\omega,t) = \bar{V}\sin(\omega t + \varphi) \quad (3)$$

$\bar{I}$ = AC current amplitude
$\bar{V}$ = AC voltage amplitude
υ = frequency
ω = angular frequency
φ = phase angle/shift

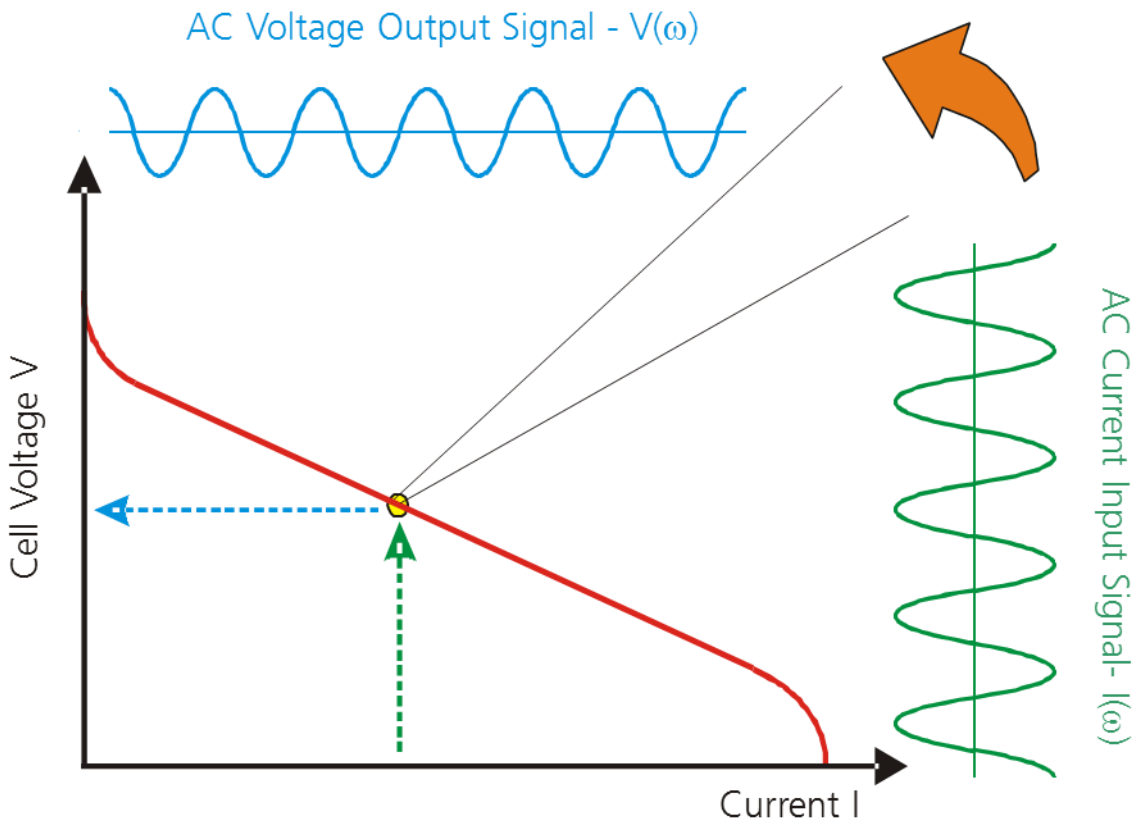

Figure 1: Input / Output signal of electrochemical impedance spectroscopy (EIS)

The impedance $Z(\omega)$ of an electrochemical component in the time domain is defined as ratio of voltage and current signal:

$$Z(\omega) = \frac{V(\omega,t)}{I(\omega,t)} = \frac{\bar{V}\sin(\omega t+\varphi)}{\bar{I}\sin(\omega t)} = |Z| \cdot \frac{\sin(\omega t+\varphi)}{\sin(\omega t)} \quad (4)$$

The Fourier analysis converts a signal from its original domain (often time or space) to a representation in the frequency domain and vice versa:

$$Z(\omega) = \frac{FFT\{V(\omega,t)\}}{FFT\{I(\omega,t)\}} = |Z|\, exp(i\varphi) = |Z|\cos(\varphi) + |Z|\, i\sin(\varphi) = Z' + i \cdot Z'' \quad (5)$$

The magnitude or the modulus of the impedance can be expressed:

$$|Z(\omega)| = \sqrt{Z'(\omega)^2 + Z''(\omega)^2} \quad (6)$$

$$tan\varphi(\omega) = \frac{Z''(\omega)}{Z'(\omega)} \quad (7)$$

Z' = real part of impedance

Z'' = imaginary part of impedance

$i^2 = -1$, imaginary unit property

The magnitude and the phase angle of the impedances of the cell/stack components change with the frequency. Therefore by varying the frequency of the excitation signal, the impedances of the studied electrochemical system can be determined as a function of frequency.

3 Test Equipment and Set-up

The impedance spectra can either be measured with alternating current (galvanostatic) or alternating voltage (potentiostatic) excitation input signal. If tests have to be performed in potentiostatic mode, an AC voltage waveform generator is needed. Otherwise, for galvanostatic test conditions, an AC current waveform generator is used. Furthermore, an AC voltage / current waveform analyzer (or frequency response analyzer, FRA) is required for recording the response of the cell or repeat unit. For measurements under DC operating current, an electrical load (fuel cell) or an additional power supply (electrolysis) is necessary. Figure 2 to Figure 5 show the generic set-ups for the testing of either cells or stacks in fuel cell (SOFC) or electrolysis (SOEC) mode. In SOFC mode for single cell and short stacks an additional voltage supply maybe needed, e.g. to overcome voltage drops in the hot current wires. In SOEC mode the voltage supply is necessary in order to impose the electrolysis voltage on the SOEC cell/stack object. In this case the polarity of the cell/stack has to be reversed in the test setup compared to the SOFC mode in order to reverse the current direction. For stack measurements the current is always applied to the whole stack whereas the voltage probes can either be connected to the complete stack or are just taken from the repeat unit of interest. The latter case has the advantage to examine the electrochemical behavior of individual repeat units of the stack. It is advised to minimize all kinds of high frequency artefacts, e.g. use twisted pair both for current and voltage probes, make sure that the voltage probes are perpendicular to the current probes etc.

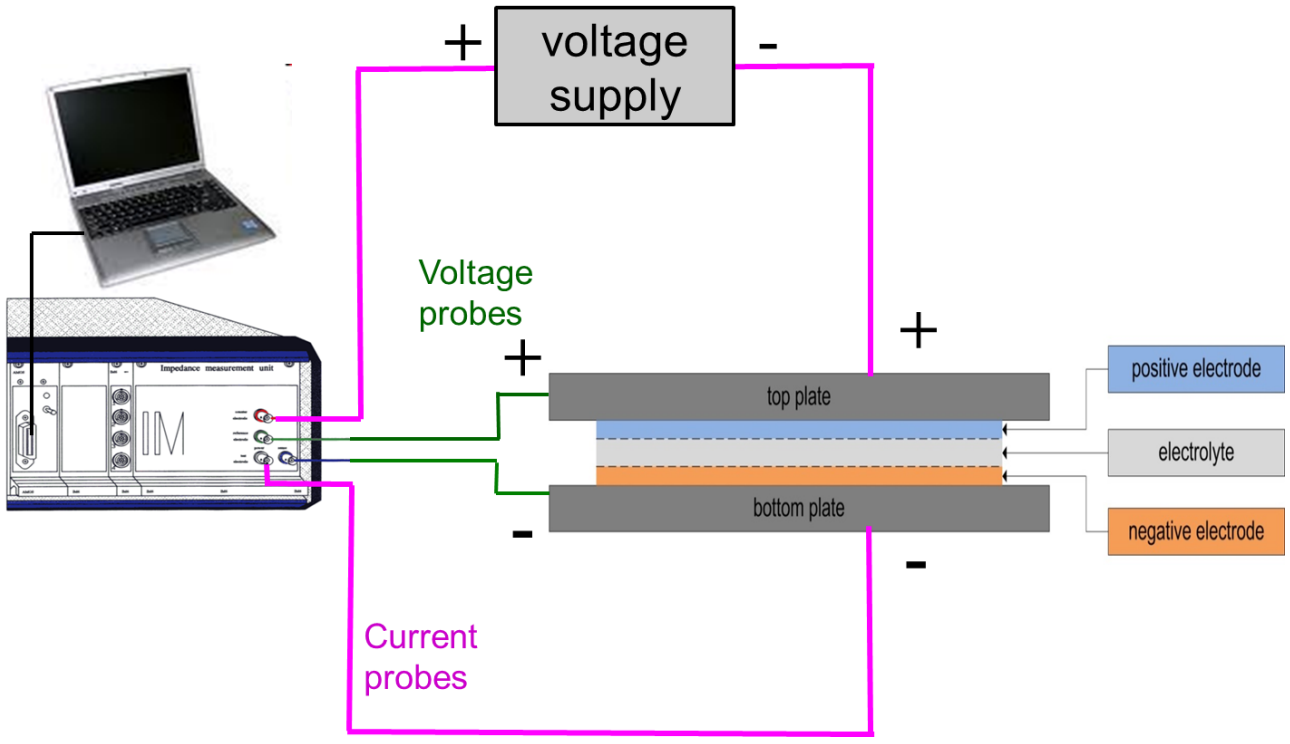

Figure 2: Set-up for electrochemical impedance spectroscopy of an SOFC cell

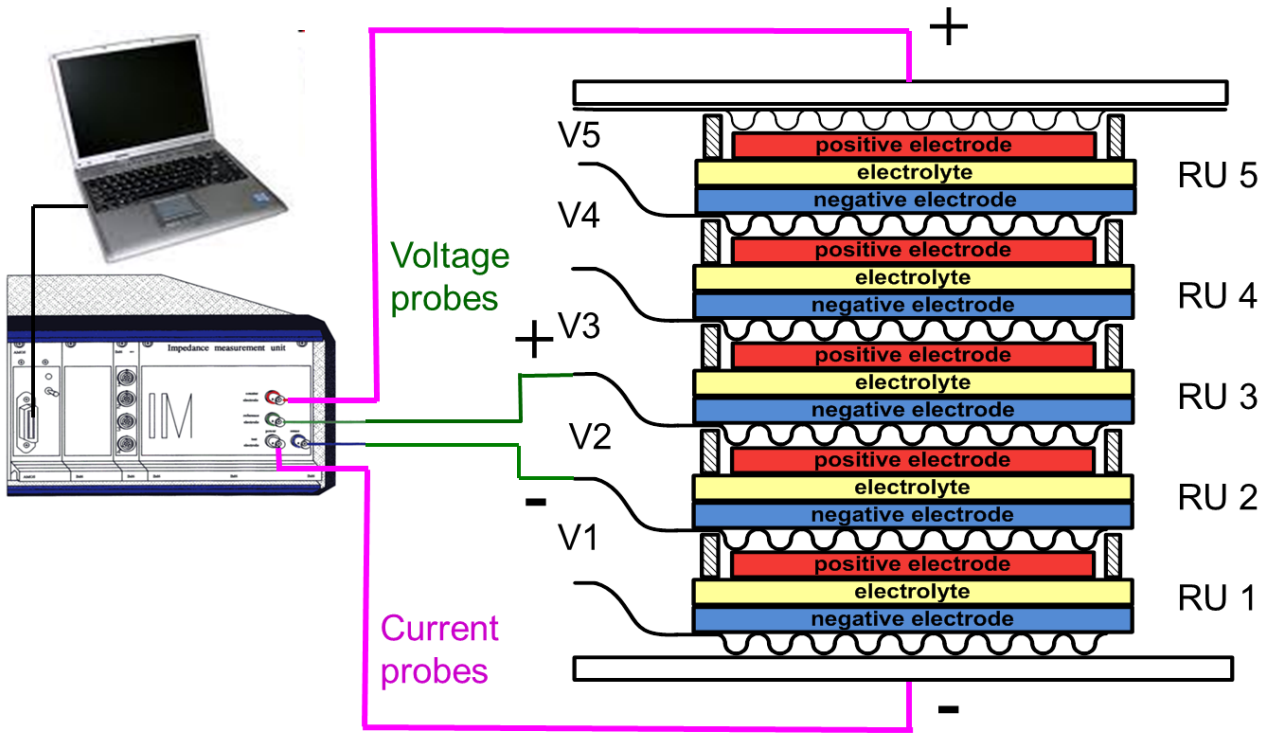

Figure 3: Set-up for electrochemical impedance spectroscopy of an SOFC stack

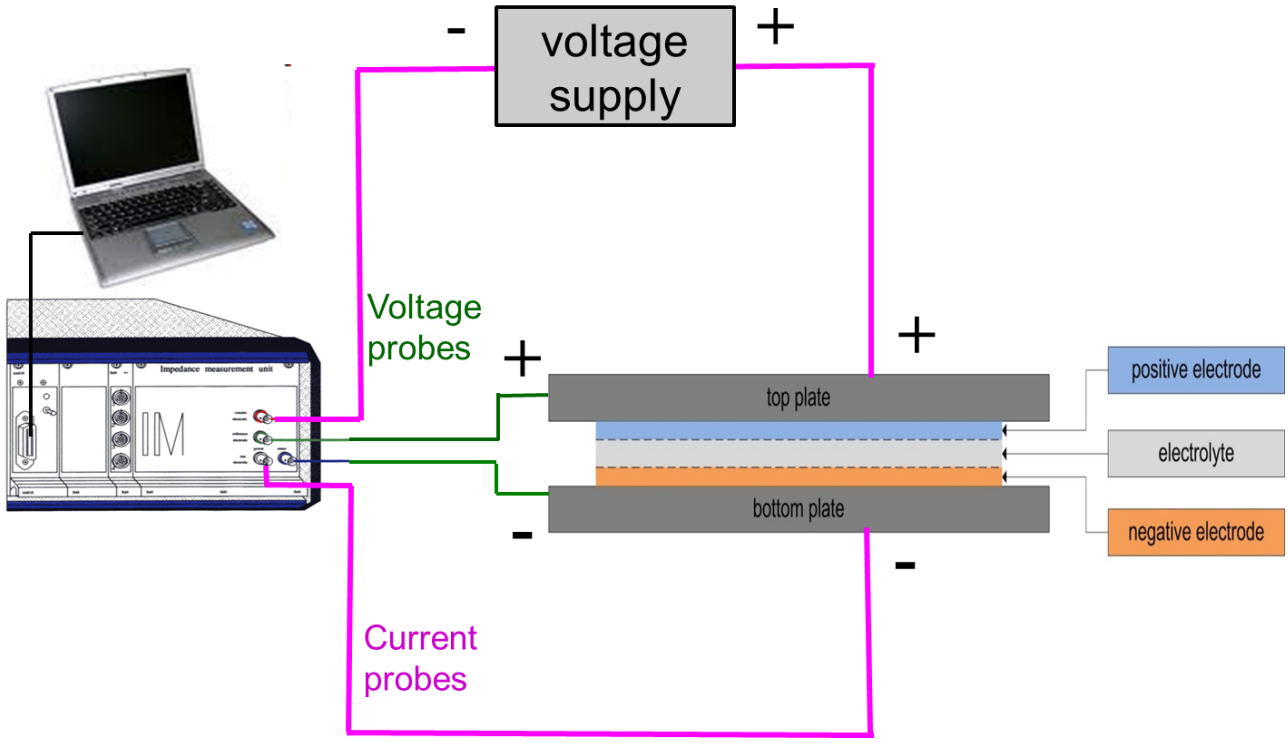

Figure 4: Set-up for electrochemical impedance spectroscopy of an SOEC cell

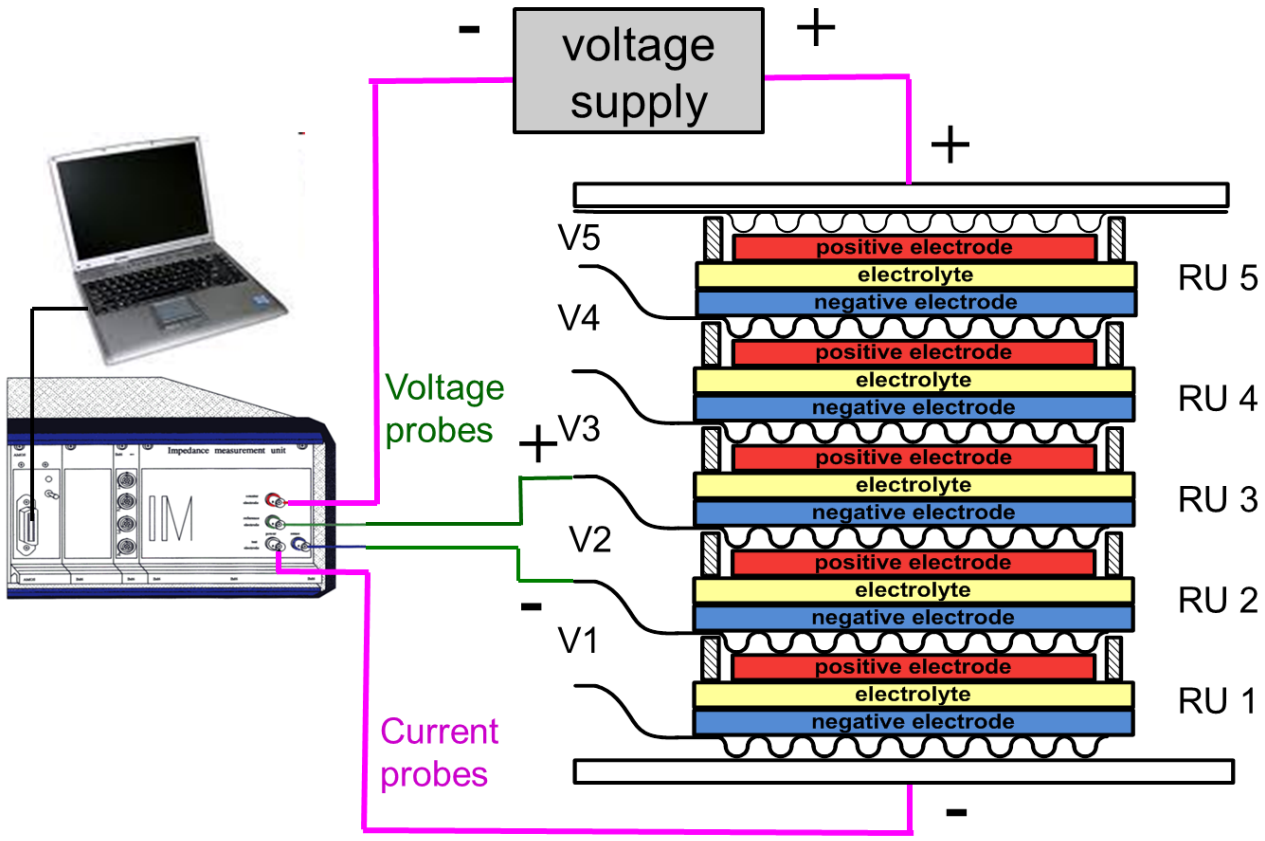

Figure 5: Set-up for electrochemical impedance spectroscopy of an SOEC stack

4 Test Input Parameters (TIPs)

There are two types of test inputs: variable and static. The first type may vary during the duration of the TM while the second type does not vary during the overall duration of the TM. The impedance spectra are usually measured in galvanostatic mode at a given constant DC current operating set point and with an alternating current input excitation signal. Another option is perform the measurement at a given direct voltage with an alternating voltage input excitation signal to the test object (potentiostatic mode). Table 1 lists all relevant static input parameters for performing electrochemical impedance spectra in galvanostatic mode. The parameters for potentiostatic mode are added in brackets. Table 2 shows the corresponding dynamic parameters which are varied during the measurement in galvanostatic mode (parameters for potentiostatic mode are added in brackets).

Table 1: Static test input parameters for electrochemical impedance spectroscopy

Description of quantity	Symbol	Unit often used	SI Unit
Active electrode area	A	cm^2	m^2
Compression force applied onto the cell/stack	F_{compr}	N	N
Flow rate of component *i* in the negative electrode gas stream at cell/stack inlet	$f_{i,neg,in}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$

Flow rate of component *i* in the positive electrode gas stream at cell/stack inlet	$f_{i,pos,in}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$
Flow rate of the negative electrode gas stream at cell/stack inlet	$f_{neg,in}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$
Flow rate of the positive electrode gas stream at cell/stack inlet	$f_{pos,in}$	nlpm, slpm $l_n\ min^{-1}$, $l_s\ min^{-1}$	$m^3\ s^{-1}$
Electrical direct current through the cell/stack	I	A	A
Electrical current density through the cell/stack	j	$A\ cm^{-2}$	$A\ m^{-2}$
Amplitude of alternating current in galvanostatic mode	$\bar{I}$	A	A
(Direct voltage of the cell/stack in potentiostatic mode)	(V)	(V)	(V)
(Amplitude of alternating voltage in potentiostatic mode)	$(\bar{V})$	(V)	(V)
Number of measuring periods for each measuring point for EIS spectra	k	-	-
Number of repeating units in the stack	N	-	-
Number of measuring points per decade for EIS spectra	n	-	-
Temperature of the pre-heater for preheating the negative electrode gas stream	$T_{PH,neg}$	°C	K
Temperature of the pre-heater for preheating the positive electrode gas stream	$T_{PH,pos}$	°C	K
Temperature of the oven	T_{oven}	°C	K
Minimum frequency for EIS spectra	υ_{min}	Hz	Hz
Maximum frequency for EIS spectra	υ_{max}	Hz	Hz
Mole fraction of component *i* in the negative electrode gas stream at cell/stack inlet	$x_{i,neg,in}$	-	-
Mole fraction of component *i* in the positive electrode gas stream at cell/stack inlet	$x_{i,pos,in}$	-	-

Table 2: Variable test input parameters for EIS

Description of quantity	**Symbol**	**Unit often used**	**SI Unit**
Frequency	υ	Hz	Hz

5 Test Output Parameters (TOPs)

Table 3 lists the test output parameters that are directly achieved by electrochemical impedance spectroscopy in galvanostatic mode. The parameters for potentiostatic mode are added in brackets.

Table 3: Test Output Parameters from EIS

Description of quantity	Symbol	Unit often used	SI Unit
Phase angle	φ	°	rad
Direct voltage of the cell in galvanostatic mode	V_{cell}	V	V
Direct voltage of repeating unit (RU) i in the stack in galvanostatic mode	$V_{RU,i}$	V	V
Direct voltage of the stack in galvanostatic mode	V_{stack}	V	V
(Direct current of the cell in potentiostatic mode)	(I_{cell})	(A)	(A)
(Direct current of repeating unit (RU) i in the stack in potentiostatic mode)	$(I_{RU,i})$	(A)	(A)
(Direct current of the stack in potentiostatic mode)	(I_{stack})	(A)	(A)
(Area specific) Impedance	Z	Ω, (Ω cm^2)	Ω
(Area specific) Modulus of impedance	$\|Z\|$	Ω, (Ω cm^2)	Ω
(Area specific) Real part of impedance	Z'	Ω, (Ω cm^2)	Ω
(Area specific) Imaginary part of impedance	Z''	Ω, (Ω cm^2)	Ω

6 Derived Quantities

The quantities listed in Table 4 are important and commonly used values calculated from input and output parameters. Additional derived quantities are described in the test module TM 00: “General SOC Testing Guidelines” [3].

Table 4: Derived quantities

Description of quantity	Symbol	Unit often used	SI Unit
(Area specific) low frequency resistance	R_{LF}	Ω, (Ω cm^2)	Ω
(Area specific) total oroverall resistance	R_{tot}	Ω, (Ω cm^2)	Ω
(Area specific) high frequency resistance	R_{HF}	Ω, (Ω cm^2)	Ω
(Area specific) ohmic resistance	R_{ohm}	Ω, (Ω cm^2)	Ω

7 Test Procedure

7.1 Critical parameters and parameter controls

The following test conditions shall be determined in advance by conducting preliminary tests when this test method is used:

1) DC current
   EIS can be measured at open-circuit voltage and/or under electric load. A spectrum measured at OCV always means a change of the operation mode between SOFC and SOEC as the AC sinusoidal excitation signal has both positive and negative amplitude. Therefore it is recommended to perform the measurement at low DC current in the range of the AC amplitude to ensure performing the test in the desired operation mode. Measurements with higher DC current, e.g. at operation current density, are used to understand the different processes occurring under load. For electrolysis measurements the external current must be negative, therefore a DC current source is needed.

2) Amplitude of excitation signal
   It is possible to excite either an alternating current or voltage. The amplitude of an AC input signal for the measurement should be high enough to generate a corresponding response signal with a high signal to noise ratio, but not too high in order to avoid measuring the spectrum in a nonlinear current - voltage response region. For using an AC voltage input signal the average amplitude per cell/RU is obtained by dividing the total voltage amplitude with the number of cells/RUs in series. It should be noted that in this case the AC voltage amplitudes applied on each RU could be different. The recommended perturbation amplitude for an AC current excitation signal is 3 - 30 mA/cm^2 and for an AC voltage excitation signal is 10 - 30 mV per cell depending on the system noise.

3) Measuring range of frequencies
   The highest frequency should be high enough to identify the ohmic resistance (about 100 kHz) and the lowest frequency should be low enough to include the potential effects of gas diffusion and gas conversion in the cell/stack (about 30 mHz).

4) Sweep mode
   It is recommended to start the measurements with high frequencies to get fast results and see directly if the measurement gives reasonable results. Afterwards sweep to lower frequencies.

5) Number of measuring points
   Four to twenty points per order of frequencies (to be distributed evenly as logarithms, if possible) are required; they shall be numerous enough to identify clearly the geometry of impedance plots. If possible avoid the fundamental and harmonics of the electrical grid frequency.

6) Number of measuring periods
   The measurement of the input signal is the average over more than one sine period. The larger the number of periods imposed, the longer the measurement will take. It is recommended to find a compromise between acceptable measuring time and precision.

7.2 Preconditioning of the stack

Before conducting the impedance measurement, the test conditions (e.g. operating temperature, fuel gases, oxidant gases, DC current) should be established as stable input parameters provide lower voltage fluctuations. It is important to precondition the stack until the temperature is stabilized. Especially when measuring spectra at high current densities a sufficient holding time is necessary after the current is increased to the set point in order to achieve thermal equilibrium.

In SOEC mode, special attention should be paid to the noise of voltage signals caused by insufficient stability in steam supply. The operation parameter of the steam generator should be optimised to reduce the noise to an acceptable level before starting the impedance measurement.

7.3 Measurement of the electrochemical impedance spectrum

The test shall be conducted using the following procedure:

1) Connect your cell/stack test object to the EIS system according to the required test mode (SOFC or SOEC) (see Chapter 3).
2) EIS can be measured at open-circuit voltage and/or under DC electric load. In the latter case increase the current stepwise to the set point. Precondition the cell/stack in order to achieve thermal equilibrium.
3) Verify that a steady state of your cell/stack in the test station has been reached. Moreover, voltage fluctuations should be kept as low as possible by ensuring stable input parameters, e.g. gas flow rates and electrical current load.
4) Superimpose AC sinusoidal waves of current or voltage at a characteristic (middle) frequency (e.g. 100 Hz) and make sure that a corresponding sinusoidal output signal is generated.
5) Start the measurement. Sweep the AC sinusoidal waves within the prescribed frequency range and measure the impedance at each selected frequency.
6) Save the measured data on a reliable data storage medium.

As an option, the validity of the impedance spectrum may be verified by using appropriate validation relations such as the “Logarithmic Kramers-Kronig (KK)” or “Z-hit” transform. These methods allow detecting violations of the EIS fundamentals of the examined system and the reconstruction of non-affected spectra, if the violations are not too strong [4].

8 Data Post Processing and Representation

In an EIS spectrum the directly achieved output parameter is the sinusoidal voltage (galvanostatic) or the sinusoidal current (potentiostatic). Moreover, the phase shift between the excitation signal and the corresponding response signal is measured directly as an output parameter. It is possible to obtain an electrochemical impedance spectrum by calculation of the corresponding impedances (see equation 4). One way is to calculate the total impedance as a function of frequency. Another possibility is to divide the total impedance (Z) into the imaginary part (Z′′) and the real part (Z′). State-of-the-art impedance analysers contain powerful software packages, which directly supply these derived quantities as output parameters. Therefore, these impedance values can be treated as test output parameters (see Table 3).

There is more than one way to illustrate the results of impedance spectra in order to interpret the processes in the cell/stack. A Bode plot shows for example the phase angle and the modulus of

impedance (see Figure 6) as a function of frequency. Another option is to plot the real and imaginary part (see Figure 7) as a function of frequency. Assuming the impedance reaches a constant level at low frequencies, the low-frequency resistance R_{LF} can be easily read from this graph. This represents the overall impedance of the test object, the ASR (area specific resistance). The lowest point of the impedance shows the high-frequency resistance R_{HF} which can be seen as the ohmic resistance of the cell/stack. The changes of the phase angle and the slope of the impedance are related to the different loss processes appearing at different frequency ranges.

In a Cole-Cole diagram - often also called Nyquist diagram - the conjugated imaginary and real parts of the impedance are plotted (see Figure 8). In this case, the low-frequency resistance R_{LF} is given by the (second) intersection of the curve with the x axis. The intersection of the tangent drawn to the curve with the x axis shows the value of R_{HF}. The difference of the high frequency resistance and the low frequency resistance gives the non-ohmic resistance of the cell/stack. This value usually contains the polarization impedances and the gas conversion impedances of the positive and negative electrodes. In the Cole-Cole diagram the arcs are caused by frequency dependent processes, e.g. the electrochemical process at the electrodes and gas concentration processes of the electrodes.

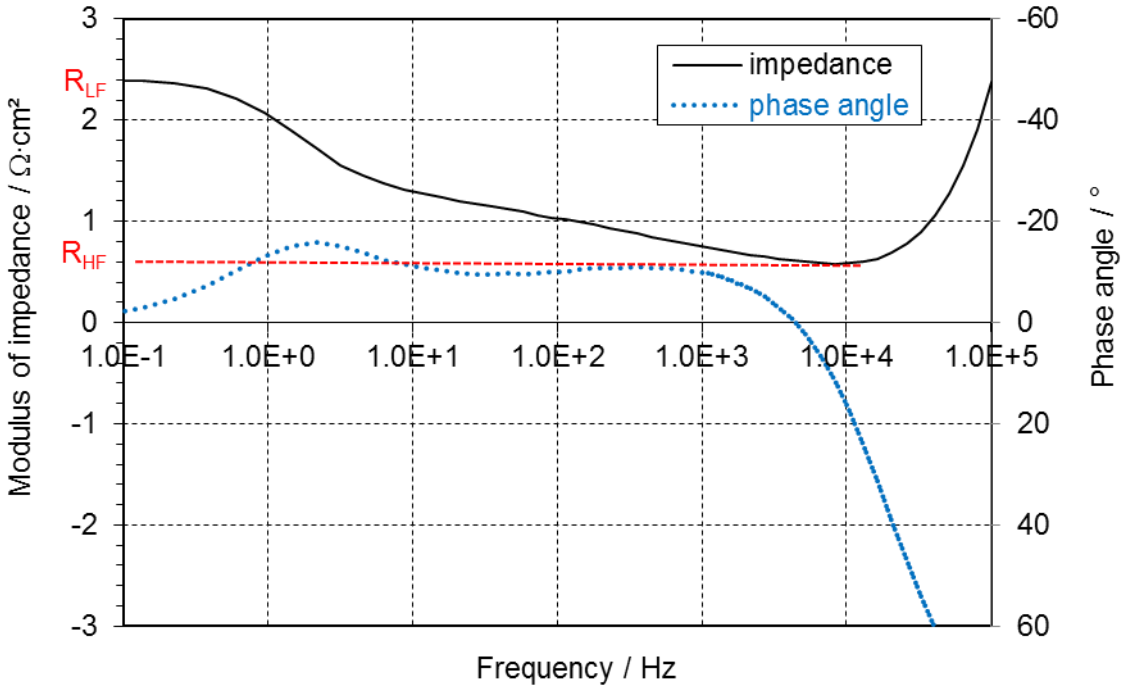

Figure 6: Bode plot representing the modulus of impedance and phase angle vs. frequency

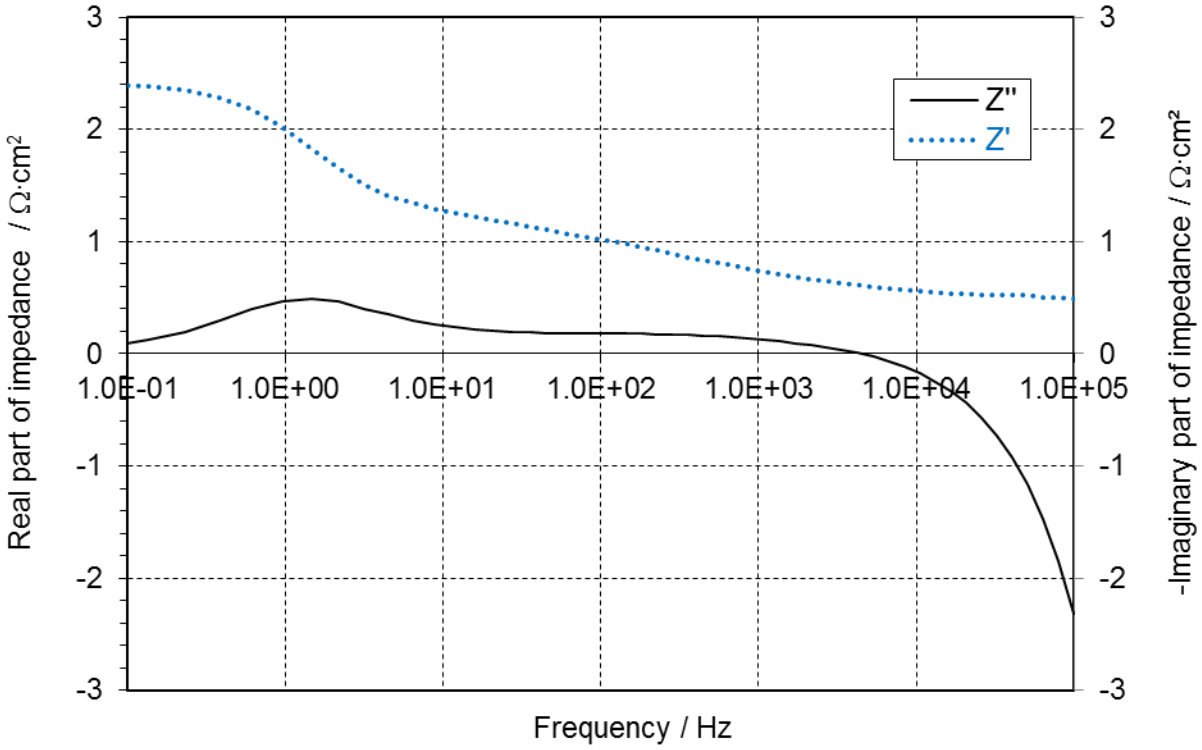

Figure 7*: Bode plot representing real and imaginary part of impedance vs. frequency*

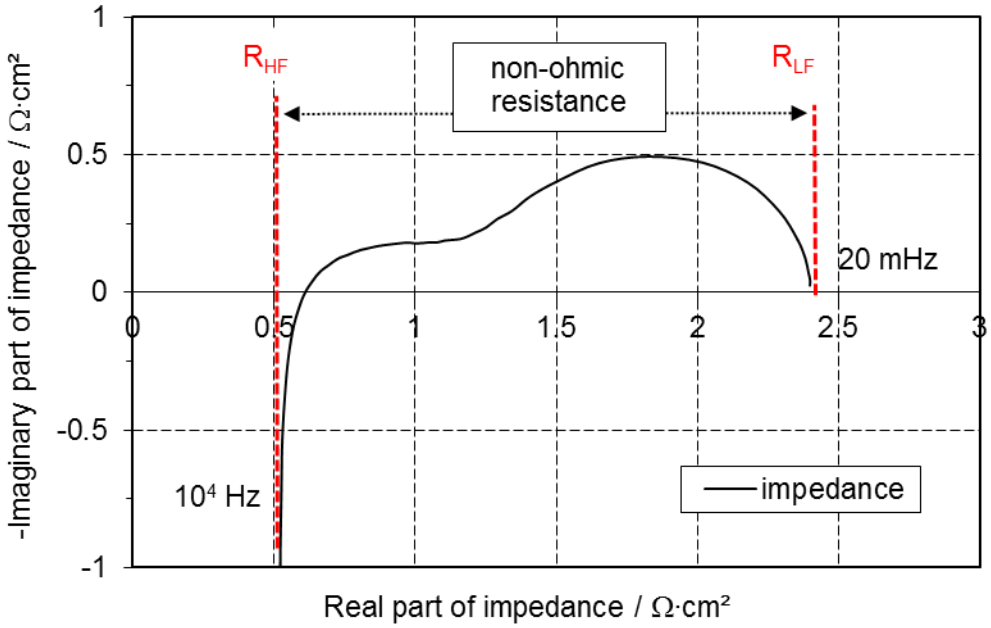

Figure 8: Cole-Cole plot representing imaginary part vs real part of impedance

The physicochemical and electrochemical processes taking place in a fuel/electrolysis cell or stack repeat unit can be modeled as an equivalent circuit consisting of passive elements such as resistors,

capacitors and inductances. Factually, these processes are distributed in space and time hence special circuit elements describing these realistic phenomena are usually taken into consideration. For instance, the Warburg element is often employed to represent the gas diffusion impedance of the SOC electrodes while the generalized constant phase element (CPE) usually replaces the ideal capacitor. Each element of the equivalent circuit represents a physicochemical or electrochemical process taking place in the cell/stack layer and is excited at a particular characteristic time. There are many different equivalent circuit models (ECMs) which are described in literature, for example in [5], [6], yet there is discrepancy on how these should be chosen/built. Different equivalent circuit models have shown to have virtually identical frequency dependent impedance behaviour.

After choosing a suitable equivalent circuit model, initial values are assigned to the elements in the model. These values can be determined in different ways. The starting values for the model can be read out from the Cole-Cole or Bode plot. The initial values are provided as input to the simulation model. Using complex nonlinear least squares (CNLS) algorithm, software can generate a curve (which is referred as a "fit") for simulating the experimental result. At the end of the simulation, the values for the various resistors, capacitors and the inductor are identified.

Results from impedance spectra fitting should be analyzed with caution. Firstly, they represent complicated electrochemical phenomena taking place inside the layers of the cell/stack unit, which have often not been completely understood. Secondly, the spectra are usually very sensitive to measuring conditions especially temperature, current and gas composition. Thirdly, disturbances such as high frequency disturbance from measuring lines influence or handicap the measurement. Fourthly, fitting of the spectra to the model is not error free – the nature of the curve with the overlap between the different impedance arcs (i.e. the frequency overlap between different electrochemical processes) as well as human induced error can give different results even when a single curve is being fitted twice by the same person. Because of these reasons, it is sometimes more advisable to use the direct results from the EIS spectra to analyze the impedance changes in relation to the different cell/stack layers, operating conditions or as a function of time.

9 Differences to Existing Procedures

Up to now only a brief description for measuring electrochemical impedance spectra on SOFC cells/stacks is given in the IEC document “IEC 62282-7-2, Part 7-2” [1]. This document describes the procedure for measuring EIS spectra very briefly and the presentation of the results with Cole-Cole plots. Another document describes several test methods (voltammetry, potentiometry and electrochemical impedance spectroscopy) for polymer electrolyte membrane stacks [2]. This document includes the setup of the test, the procedure and the data representation specifically for low temperature fuel cell stacks.

In contrast to the above mentioned documents, the present test module TM04 describes much more detailed the electrochemical impedance spectroscopy for solid oxide cells and stacks. The basic principles of EIS, the test equipment and setup, the relevant test input and output parameters, the derived quantities, the test procedure for measuring EIS spectra are reported. Moreover, the data post processing and representation of the results with all important diagrams and interpretation of the results are explained. Finally, the present test module document addresses both the fuel cell (SOFC) and the electrolysis (SOEC) operation modes.

10 Bibliography

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